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BOND ALTERNATION IN THE INFINITE POLYENE: EFFECT OF

LONG RANGE COULOMB INTERACTIONS

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ABSTRACT

We investigate the effects of long-range Coulomb interactions on bond and site dimerizations in a one-dimensional half-filled band. It is shown that the ground state broken symmetry is determined by two sharp inequalities involving the Coulomb parameters. Broken symmetry with periodicity $2k_F$ is guaranteed only if the first inequality (downward convexity of the intersite potential) is obeyed, while the second inequality gives the phase boundary between the bond-dimerized and site-dimerized phases. Application of these inequalities to the Pariser-Parr-Pople model for linear polyenes shows that the infinite polyene has enhanced bond alternation for both Ohno and Mataga-Nishimoto parametrizations of the intersite Coulomb terms. The possible role of distant neighbor interactions in photogeneration experiments is discussed.

I. Introduction

Theoretical modelling of polyacetylene, and by implication, of related π-conjugated polymers, has recently seen both enormous advances and continuing controversies.[1] A central issue in these controversies is the relative importance of direct Coulomb interactions between electrons vis-a-vis the electron-intersite phonon coupling that leads to the observed bond-alternation in polyacetylene. Several recent experiments have emphasized the strong role of Coulomb interactions,[2-4] and indeed, even suggest that the optical gap in the pristine polymer may be dominated by electron-electron interactions.[2,5] Since the original theory of bond-alternation in polyacetylene is based on the one-electron Peierls model, this experimental information has led to considerable theoretical effort to determine the ground state broken symmetry in a one-dimensional half-filled band with direct interactions among electrons.[1] An additional motivation for such studies is that similar investigations can also lead to a better understanding of the various phase-transitions that occur in quasi-one-dimensional charge-transfer solids[6] as well as the quasi-two-dimensional Bechgaard salts[7] with band fillings other than half.

Despite the intense recent efforts, definitive results have been obtained only for short-range electron-electron interactions[8-12] (typically on-site and nearest neighbor repulsion). In contradiction to earlier theoretical results, both recent approximate[11,12] and numerical studies[8-10] agree that short-range Coulomb interactions can enhance (up to certain maximum values) the bond-alternation relative to that obtained in the uncorrelated limit. In particular, with just an on-site electron repulsion U and a nearest neighbor repulsion V_1, it is

now known that for $V_1 = 0$, U enhances bond alternation up to $U \sim 4t_o$, while for $V_1 > 0$, enhanced bond alternation occurs for $V_1 \leq \frac{1}{2}U$. Although these short range results are significant, the importance of determining the effects of long-range Coulomb interactions cannot be overestimated. Firstly, the peculiar geometry of π-conjugated polymers (bond angle of $120°$ around each carbon atom) and the short C-C bond lengths (~ 1.35 A and ~ 1.45 A) inply that the Coulomb interactions may decay quite slowly. Indeed, the various Pariser-Parr-Pople (PPP) parametrizations[13] show exactly such slow decay, and even fifth- or sixth-neighbor interactions are comparable to or only slightly smaller than the nearest neighbor transfer integral. Secondly, existing theoretical results already indicate that the use of effective short-range interactions to approximate long range forces does not yield the correct ground state broken symmetry.[8,9] Thirdly, the present approximate methods for long-range interactions[14-16] are for the PPP model only, with specific parameters thought to be applicable to the gas phase of linear polyenes. Even with these specific parameters, the approximate methods predict very contradictory results, and it is therefore important to have accurate benchmark results against which the approximate methods can be tested. Extrapolations based on numerical calculations on finite chains[17] cannot be definitive, since by including more distant Coulomb interactions in larger systems these calculations effectively deal with different Hamiltonians for finite systems with different sizes. Furthermore, such calculations cannot yield a general solution, since each change of parameters requires an entirely new set of calculations. Finally, all the above calculations[14-17] assume at the outset broken symmetries with a periodicity $2k_F = \pi/a$ (a = lattice

spacing) and this is not necessarily correct. Since no simple band picture applies at moderate to strong electron correlations, and there is no well defined k_F (Fermi wave vector), why should $2k_F$ broken symmetry occur at all?

In the present paper, we solve the problem of the ground state broken symmetry in a one-dimensional half-filled band with arbitrarily long-range Coulomb interactions. A brief presentation has been made earlier.[13] Unlike the previous approaches,[14-17] we impose no restriction on either the magnitudes or the spatial range of Coulomb interactions, except that these are repulsive and there is a continuous decay. We cover a complete class of models that includes both those favored by chemists (e.g., PPP) and those favored by physicists (SSH and Peierls-extended Hubbard). We discuss a mechanism for the $2k_F$ broken symmetries for arbitrary electron correlations and derive a sharp inequality that provides a sufficient condition for $2k_F$ periodicity to occur. We further derive a second inequality that then gives the phase-boundary between the $2k_F$ bond order wave (BOW) which favors bond alter-nation and the $2k_F$ charge density wave (CDW) which favors equal bond lengths. Non-$2k_F$ periodicity may occur if the first of these inequali-ties is violated. Finally, we apply our results to the PPP model, show that none of the approximate methods yield complete results, and resolve the controversies among existing predictions. The implications for polyacetylene are then discussed.

II. Theoretical Models and Broken Symmetries

The particular class of models of interest here are described by the Hamiltonian

$$H = H_{1-e} + H_{e-e} \tag{1a}$$

$$H_{1-e} = \sum_{i,\sigma} [t_o - \alpha(y_i - y_{i+1})][c^\dagger_{i\sigma} c_{i+1,\sigma} + c^\dagger_{i+1,\sigma} c_{i\sigma}] + \beta \sum_i n_i q_i \tag{1b}$$

$$H_{e-e} = U\sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,j} V_j n_i n_{i+j} \tag{1c}$$

Here H_{1-e} contains all the one-electron terms including the intersite $(y_i - y_{i+1})$ and intrasite (q_i) electron-phonon couplings. The intrasite electron-phonon coupling is not relevant for systems like polyacetylene, but is relevant for applications to molecular solids. We have not included the phonon elastic energy, as we are interested only in the unconditional broken symmetries, i.e., those that occur in the limit of $\alpha, \beta \to 0+$. The many-electron term H_{e-e} includes both the on-site and intersite Coulomb repulsion parameters U and V_j, with $n_i = \sum_\sigma n_{i\sigma}$,

where $\sigma = \pm 1$ refer to up ($\uparrow$) and down ($\downarrow$) spins of electrons. The only restriction we have on the Coulomb terms is the condition of continuous decay, viz., $U > V_1 > V_2 > \cdots 0$. Notice that the PPP Hamiltonian is usually written slightly differently from Eq. 1(c). This difference is illusory, as one can easily show that the present form shifts all energies by a constant.

It is useful at this stage to describe the various broken symmetries one can have for the Hamiltonian (1) in the half-filled band. Broken symmetries having periodicity $2k_F$ and familiar from the pure electron-phonon (Peierls) models include:

(i) the $2k_F$ bond order wave (BOW) with a modulation of the bond order $\frac{1}{2} \sum_\sigma < c_{i\sigma}^+ c_{i+1,\sigma} + c_{i+1,\sigma}^+ c_{i\sigma} >$, and hence the bond length for $\alpha > 0$ (note

that the BOW is also referred to as the <u>inter</u>site charge density wave), (ii) the $2k_F$ <u>intra</u>site charge density wave (CDW), with a periodic modulation of the site charge density, and (iii) the $2k_F$ spin density wave (SDW) with periodic modulation of the spin density. The BOW and the CDW correspond to broken <u>discrete</u> symmetries and therefore can lead to long-range order, whereas the SDW involves a broken continuous symmetry (spin orientation) and therefore has only algebraic, rather than long-range order. Importantly, from studies of both the Hamiltonian (1)[8,9] and of the spin-Peierls system[19] (which is the $U \to \infty$ limit of (1)), it is known that the $2k_F$ SDW coexists with the $2k_F$ BOW even up to $U \to \infty$. Thus here we can focus solely on the competition between the BOW and CDW. Finally, although it is <u>not</u> familiar from the pure electron-phonon system for certain ranges of the nonzero Coulomb interactions we can have a non-$2k_F$ CDW; significantly this can only occur if V_2 (or other higher V_j's) $\neq 0$ and thus is missed in simple extended Peierls-Hubbard models.

Our results can be summarized briefly. We show that a $2k_F$ periodicity is unconditional only if the intersite part of the potential is downward convex, i.e.,

$$V_{j+1} + V_{j-1} > 2V_j \tag{2}$$

while if Eq. (2) is invalid, a non-$2k_F$ CDW may occur. If Eq. (2) holds, then the dominating ground state broken symmetry is given by a second inequality,

$$\sum_j V_{2j+1} \lessgtr \tfrac{1}{2}U + \sum_j V_{2j} \tag{3}$$

If the left hand side of (3) is smaller a $2k_F$ BOW results, while for a smaller right hand side the ground state has a $2k_F$ CDW. Near the equality the BOW and the CDW can coexist.

III. The Real Space Mechanism of Broken Symmetry

Since the momentum space (band) picture is lost for moderate to strong Coulomb correlations, it is most natural to seek a physical understanding of the mechanism of broken symmetry in correlated systems within a real space picture. The basic tenents of the real space picture[8] are:

(i) All real space many-electron configurations are diagonal or off-diagonal with respect to the symmetry operator that is lost when the symmetry is broken. Broken symmetry implies unequal contributions to the ground state wavefunction by configurations that are off-diagonal with respect to the particular symmetry operator, but are otherwise equivalent.

In the present case, for the $2k_F = \pi/a$ periodicity, all configurations can be classified as L (left), R (right) or S (symmetric), where L and R are off-diagonal with respect to reflection between (through) the sites, corresponding to the $2k_F$ CDW (BOW).

(ii) The off-diagonal configurations can be further classified according to the extent to which they favor broken symmetry. Thus for periodicity π/a, L_1 favors left-phase most strongly, L_2 slightly less strongly and so on. Similarly, we can have R_1, R_2,... etc. Only L_1 and R_1 are unique, and we will refer to them as "extreme" configurations.

(iii) All real-space configurations are diagonal in H_{e-e} but off-diagonal with respect to H_{1-e}. The two extreme configurations can be reached, one from the other, by repeated applications of H_{1-e}, and broken symmetry is due to a barrier to perfect resonance (in the chemical sense) between L_1 and R_1. The overall barrier to resonance can be determined by inspection of only the extreme configurations, since all intermediate configurations lie along the paths (generated by H_{1-e}) connecting them. For $H_{e-e} = 0$ resonance is imperfect in infinite systems (even for 0+ couplings) because of the infinite lengths of the paths. $H_{e-e} \neq 0$ enhances (decreases) the barrier to resonance depending on whether matrix elements of H_{e-e} of intermediate configurations along all paths are higher (lower) in energy than those of the extreme pair. These observations establish our first result: electron-electron interactions will enhance a given broken symmetry if the appropriate extreme configurations form the ground state of H_{e-e} (i.e., the ground state of H at $H_{1-e} = 0$). If any other configurations have lower energy at $H_{1-e} = 0$, the broken symmetry (for some coupling strength) will be destroyed. A simple extension of this argument is as follows: if the ground state of H_{e-e} is neither of the extreme configurations that favor the $2k_F$ CDW or $2k_F$ BOW, possibility of a non-$2k_F$ CDW arises.

Simple inspection shows that the extreme configurations for the $2k_F$ CDW are

$$L_1^{CDW} = c_{1\uparrow}^+ c_{1\downarrow}^+ c_{3\uparrow}^+ c_{3\downarrow}^+ \cdots |0>$$

and R_1^{CDW}, which has sites 2, 4,... doubly occupied. For the $2k_F$ BOW, it has been shown previously[8] that

$$L_1^{BOW} = (c_{1\uparrow}^+ c_{2\downarrow}^+ - c_{1\downarrow}^+ c_{2\uparrow}^+)(c_{3\uparrow}^+ c_{4\downarrow}^+ - c_{3\downarrow}^+ c_{4\uparrow}^+) \cdots |0\rangle$$

with R_1^{BOW} having perfect spin pairings between sites 2 and 3, 4 and

5,... etc. Since for $H_{1-e} = 0$ energies depend on site occupancies only,

we arrive at the conclusion that if the ground state of H_{e-e} is the

configuration $\cdots 2020 \cdots$ (or equally, $\cdots 0202 \cdots$) then for $H_{1-e} \neq 0$ an

enhanced $2k_F$ CDW is guaranteed, while if the ground state is $\cdots 1111 \cdots$

an enhanced $2k_F$ BOW is ensured, where the numbers 0, 1 and 2 denote site

occupancies. One final point should be noted here. From the symmetry

properties of the extreme $2k_F$ CDW or $2k_F$ BOW configurations it is

obvious that an enhanced $2k_F$ CDW will destroy a $2k_F$ BOW and vice versa.

This result was obtained earlier in the absence of correlations $(U, V_j =$

0) by Kivelson[20(a)] and Su[20(b)], but as we see here, it remains valid

for arbitrary U and V_j (although the exact width of the coexistence

region may depend on the magnitude and range of U and V_j).

IV. The Ground State of H_{e-e}: An Exact Theorem

In this section we state and present the outlines of the proof of

an exact theorem:[18] if inequality (2) holds, so that the potential is

downward convex, then the ground state of H_{e-e} is the configuration

$\cdots 2020 \cdots$ if $\tfrac{1}{4}U + \sum_j V_{2j} < \sum_j V_{2j+1}$, whereas it is $\cdots 1111 \cdots$ if

$\tfrac{1}{4}U + \sum_j V_{2j} > \sum_j V_{2j+1}$.

The detailed nature of this proof is to lengthy to present here,

and we provide only a sketch to motivate its validity. We classify

configurations according to the number N_2 of double occupancies, and

write $E(N_2)$ as the energy of the particular configuration which has the

lowest energy within this class. If inequality (2) is valid, it can be shown exactly that this particular configurtion is unique and known, while if inequality (2) is not true one cannot determine the lowest energy configuration. We extend a method originally due to Hubbard for $U = \infty$ and arbitrary band fillings to the case of <u>finite</u> U and the half-filled band (and thus an equal number of 2's and 0's) to prove that within each class of configurations with N_2 double occupancies, the configuration with the lowest energy is the one in which all 2's and 0's are adjacent and alternating. $E(N_2)$ is now known exactly. For $0 \leq N_2 \leq N/4$,

$$E(N_2) = N_2 U + \sum_{j=1}^{2N_2} [N+(-1)^j (2N_2-j)]V_j + N \sum_{j=2N_2+1}^{\frac{N}{2}-1} V_j + (\frac{N}{2})V_{N/2} \quad (4)$$

while for $N/4 \leq N_2 \leq N/2$,

$$E(N_2) = N_2 U + \sum_{j=1}^{N-2N_2} [N+(-1)^j (2N_2-j)]V_j$$

$$+ \sum_{j=N-2N_2+1}^{\frac{N}{2}-1} [N+(-1)^j (4N_2-N)]V_j + \frac{1}{2} V_{N/2} [N+(-1)^{N/2}(4N_2-N)] \quad (5)$$

In both (4) and (5) the last terms, which are irrelevant for infinite systems, are indicated in anticipation of our later study of finite rings. Note that (4) and (5) limit correctly to the values $E(0) = N(V_1+V_2+V_3+\cdots)$ and $E(N/2) = \frac{1}{2}NU + 2N(V_2+V_4+V_6+\ldots)$, respectively. Simple algebraic manipulations now show that if the lefthand side in

Eq. (3) is smaller so that $E(0) < E(N/2)$, then $E(0) < E(N_2)$ for all N_2 provided Eq. (2) is true. Similarly, if the right hand side in (3) is smaller, then $E(N/2) < E(N_2)$ follows if Eq. (2) is true. This proves our theorem regarding the exact ground state at $H_{1-e} = 0$.

V. Numerical Results

The results obtained in sections III and IV are based on intuitive physical arguments and an exact theorem valid in the strong coupling limit. To confirm the heuristic arguments of section III we have performed exact numerical calculations on a ten-site ring. We present a few representative results here to show that the numerical results obey our theoretical predictions completely. To demonstrate an enhanced $2k_F$ BOW, we choose to study[21]

$$\Delta(\Delta E) \equiv \Delta E(U, V_j) - \Delta E(0) \tag{6}$$

where $\Delta E(U, V_j) \equiv E(U, V_j, t_{i,i+1} = t_o(1+(-1)^i\delta)) - E(U, V_j, t_{i,i+1} = t_o)$

and $E(U, V_j, t_{i,i+1})$ is the total <u>electronic</u> energy. Thus $\Delta(\Delta E) > 0$ implies that the Coulomb interactions enhance the $2k_F$ BOW. To investigate the $2k_F$ CDW, we evaluate the charge density structure factor,

$$S(q) = S_q = N^{-1} \sum_{j,\ell} <n_j n_{j+\ell}> e^{iq\ell a} \tag{7}$$

and study $\Delta S_\pi \equiv S_{\pi/a}(U; V_j) - S_{\pi/a}(0)$, noting that $\Delta S_\pi > 0$ implies that the Coulomb interactions enhance the $2k_f$ CDW.

The inequalities (2) and (3) are independent of the cutoff in V_j and N, with the only finite size effect being that the last term on the left hand side of Eq. (3) must have a coefficient of $\frac{1}{2}$. Altogether we

have studied more than fifty different combinations of U, $V_1, \ldots, V_5$ (the maximum physical V_j for the N = 10 system) and verified our predictions in each case; we focus here on three illustrative examples. First, we take $U < 2V_1$, and $V_j = 0$ for $j \geq 3$. For $V_2 = 0$ we have an enhanced $2k_F$ CDW according to Eqs. (2) and (3), while for $V_2^C \gtrsim V_1 - \tfrac{1}{2}U$ we predict an enhanced BOW. We have plotted both $\Delta(\Delta E)$ and ΔS_π for this case -- we take $U = 4$, $V_1 = 3$ (where $t_0 = 1$), so that $V_2^C \cong 1$ -- in Fig. 1, and we see that numerical results agree with this completely. Second, with $V_j = 0$ for $j \geq 4$, we choose values of U, V_1, and V_2 such that we have an enhanced $2k_F$ BOW initially. We now increase V_3 from 0 and expect that for $V_3^C \gtrsim \tfrac{1}{2}U + V_2 - V_1$, the system transforms to an enhanced $2k_F$ CDW. Again, the results in Fig. 2 reflect this behavior. Inequalities (2) and (3) are based on strong coupling ($t_0 \to 0$) results, and for finite values of t_0 the region of coexistence between the $2k_F$ BOW and CDW can be relatively broad. For example in Figs. 1 and 2, the coexistence region is roughly 0.5 t_0. Our inequalities will always correctly predict the dominant broken symmetry; they do not, however, preclude the coexistence of a weaker competing broken symmetry. Finally, if we take $U < 2V_1$, $V_j = 0$ for $j \geq 3$ and increase V_2 until $V_2 > \tfrac{1}{2}V_1$, we violate the downward convexity condition (2) and expect a non-$2k_f$ CDW. In Fig. 3 we have plotted S(q) from Eq. (9) for such a case and show that it indeed peaks at $q \neq 2k_F = \pi/a$. We have deliberately chosen values of U, V_j etc. close to the PPP values to demonstrate the validity of our results for realistic parameters. Inequalities (2) and (3), however, are valid for the complete range of parameters, and results for much larger parameters (with U = 10) have been presented earlier.[18]

VI. Conclusions

Application of our results to PPP-type models is straightforward, and one important consequence is that both the PPP-Ohno and PPP-Mataga Nishimoto Hamiltonians[13] yield a ground state with enhanced bond-alternation, in contradiction to previous predictions based on approximate theories. Whether the PPP models are applicable to polyacetylene is another matter altogether. However, several important points should be made.

First, as has been discussed in detail by Baeriswyl,[22] it would seem natural that the value of the spring constant K in polyacetylene should be similar to benzene and not to ethane. Thus the dimensionless electron-phonon coupling constant α^2/Kt_o is substantially smaller than that used in the noninteracting models, based on the K for ethane. Similar ideas have previously been emphasized by Misurkin and Ovchinnikov[23] and Kakitani,[24] while the magnitude of the electron-phonon coupling parameter used by Pietronero and Strässler[25] for calculations on graphite is very close to the "unbiased" value obtained by Baeriswyl.[22] If one adopts this perspective, then the observed bond-alternation in trans-polyacetylene must represent enhanced dimerization due to electron correlation.

Second, since the application of the unrestricted Hartree Fock (UHF) method to the PPP model of $(CH)_x^{15}$ does not yield the correct ground state broken symmetry, the results obtained for optical and soliton states using UHF should be reexamined. In particular, UHF techniques may fail to capture possible excitonic states.

Third, important observables are affected in _different_ ways by
Coulomb interactions. The optical gap and spin density, for example,
can be argued to vary as $U-V_1$ to leading order and are only weakly
dependent on more distant interactions. Thus it is possible to deter-
mine effective short range parameters to describe these observables
quantitatively. For other observables, however, one may well require
true solutions for excited states in the presence of long-range inter-
actions. In photogeneration, for example, the physical separation of
the electron-hole pair into charged soliton-antisoliton is strongly
dependent on the relative magnitudes of short-range and long-range
Coulomb interactions. Indeed, within the simple Peierls-Hubbard model
($V_j = 0$) charge-separation is expected for $U > 0$, but even a small V_1
can lead to exciton formation, while inclusion of a second-neighbor
interaction V_2 reduces the barrier to charge-separation somewhat. An
additional theoretical problem arises from the limitation of exact
numerical calculations to small systems.[5,17] In these systems there is
rather strong soliton-antisoliton overlap in both closed rings and open
chains (as well as strong end effects in the open chains) that would
prevent charge separation. Quantum Monte Carlo methods[9,10] cannot at
present examine the optical state, while as we have indicated here, the
approximation methods which have examined the effects of long range
interactions are of doubtful validity even for the ground state. A
major effort should be made to solve the excited state problem in
correlated states; in this regard, recent renormalization group
approaches[26] appearing promising.

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FIGURE CAPTIONS

Fig. 1. $\Delta(\Delta E)$ (solid line, zero indicated on left axis) and ΔS_π (dashed line, zero indicated on right axis) versus V_2 for $U = 4$ and $V_1 = 3$, in units of t_o. Equation (3) predicts that beyond $V_2 = 1$ (indicated by an arrow on the graph) the CDW should disappear and the BOW should appear. Due to the non-zero intersite electron-phonon coupling[21] the BOW appears slightly before V_2^c and in the region $0.5 \lesssim V_2 \lesssim 1.1$, both the BOW and CDW coexist. Note that when the plotted quantities fall below zero, there is no tendency toward the corresponding broken symmetry.

Fig. 2. $\Delta(\Delta E)$ (solid line, zero indicated on left axis) and ΔS_π (dashed line, zero indicated on right axis) versus V_3 for $U = 5$, $V_1 = 4$, and $V_2 = 1.8$. The arrow indicates the critical V_3 (0.3) beyond which the CDW should appear and the BOW disappear. The persistence of the BOW beyond V_3^c is in part due to the non-zero -- electron-phonon coupling used in measuring $\Delta(\Delta E)$.

Fig. 3. The structure factor $S(q)$ versus qa/π for $U = 4$, $V_1 = 2.5$, and $V_2 = 1.5$ and 2.0. $S(q)$ peaks at $q < 2k_F = \pi/a$ for $V_2 > V_2^c = 1.25$ and shifts to smaller q as V_2 increases.
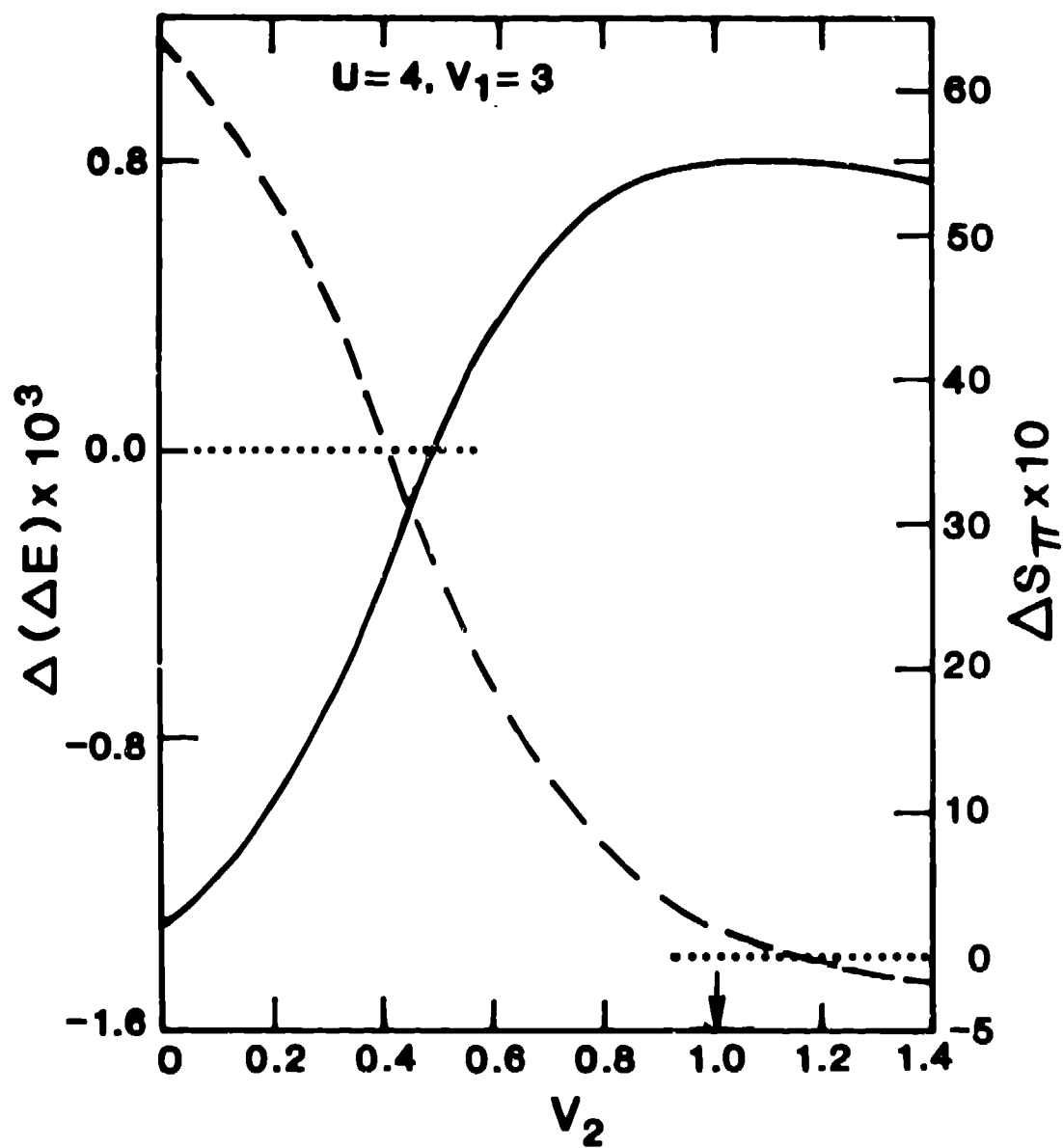
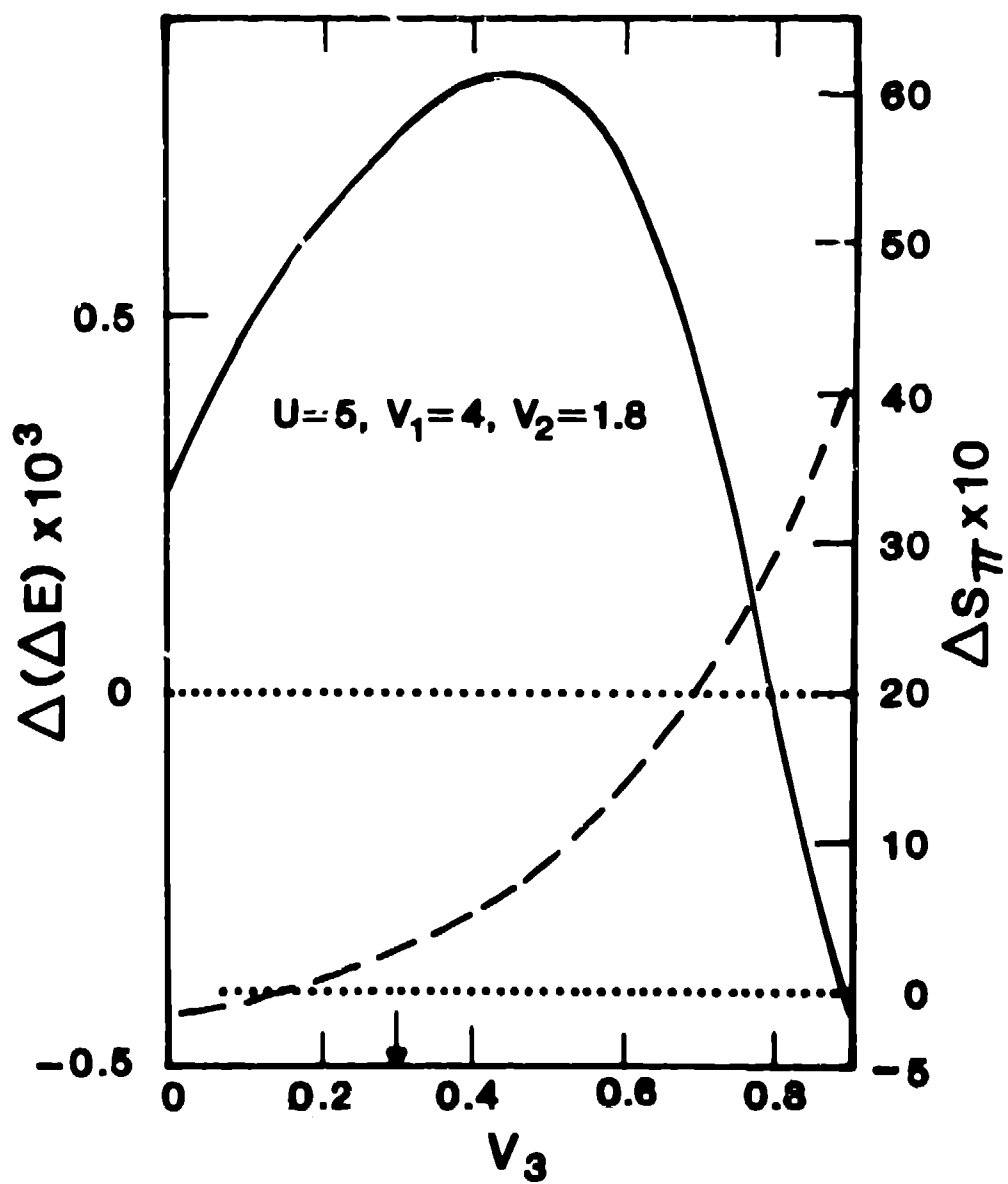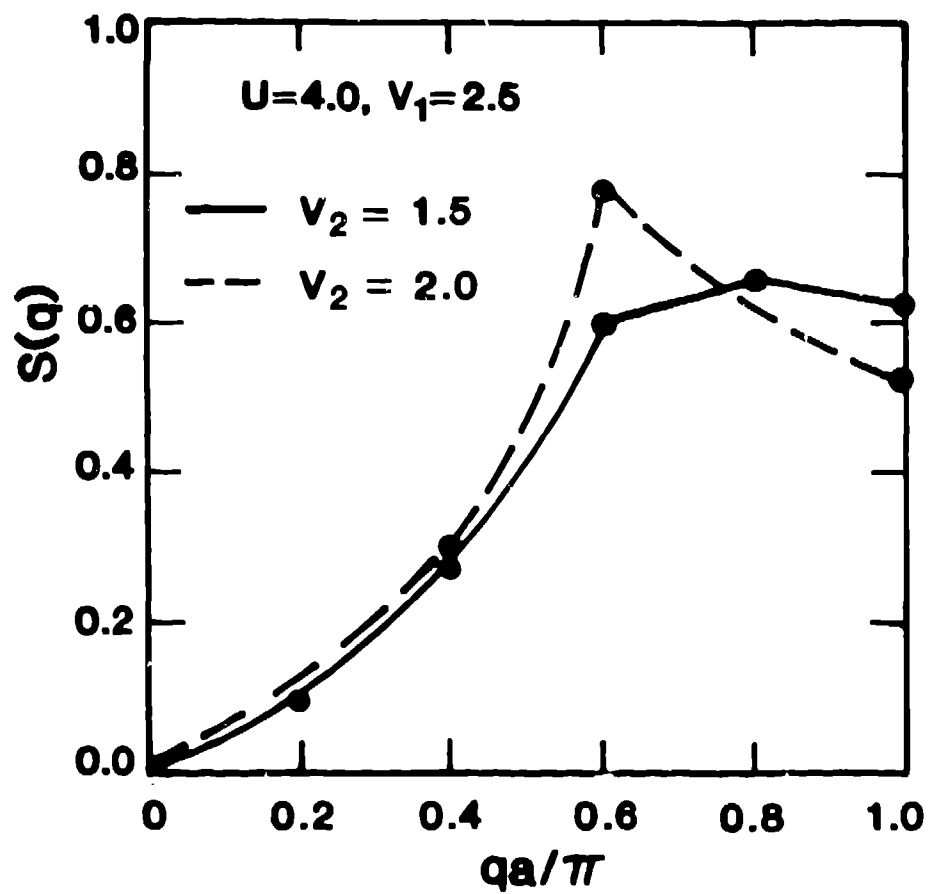Fig.1. Mazumdar and Campbell, Synthetic Metals

Fig. 2. Mazumdar and Campbell, Synthetic Metals

Fig. 3, Mazumdar and Campbell, Synthetic Metals